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## Trinuclear Nickel Complexes with Metal-Arene Interactions Supported by Tris- and Bis(phosphinoaryl)benzene Frameworks

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### Abstract

Triphosphine and diphosphine ligands with backbones designed to facilitate metal-arene interactions were employed to support multinuclear Ni complexes. Di- and trinuclear metal complexes supported by a triphosphine containing a triarylbenzene linker display diverse metal-arene binding modes. Multinuclear Ni halide complexes were isolated with strongly interacting metal centers bound to opposite faces of the coordinated arene. Upon reaction of the trinickel diiodide complex, **2**, with disodium tetracarbonylferrate, a cofacial triangulo nickel(0) complex, **4**, was isolated. The  $\text{Ni}_3^0$  cluster motif can also be supported by a *para*-terphenyldiphosphine, where a terminal carbon monoxide ligand replaces the third phosphine donor. All multinuclear complexes feature strong metal-arene interactions, demonstrating the use of an arene as a versatile ligand design element for small clusters.

Multinickel complexes have been employed for a variety of transformations.<sup>1</sup> Di- and trinickel complexes have been reported to activate, cleave, and electrochemically reduce  $\text{CO}_2$ .<sup>1a-e, 1g</sup> C–C cross-coupling chemistry has been reported at dinuclear sites as well.<sup>1f</sup> To further develop the reactivity of multinuclear Ni complexes, the development of new coordination motifs is of interest. A wide variety of multidentate ligands have been utilized to support dinuclear transition metal chemistry.<sup>2</sup> Ligand design strategies for the controlled synthesis of trinuclear complexes are less developed. Several approaches have been reported recently for targeting trinuclear complexes of Mn, Fe, Co, Cu, and Zn.<sup>3</sup>

We have employed multidentate phosphines linked by aryl-benzene bridges to support mono- and dinuclear complexes stabilized by strong metal-arene interactions.<sup>1f,4</sup> The central arene in these systems serves both as a spacer to facilitate the coordination of multiple metals by the phosphines and as a site of metal coordination with a variety of possible binding modes. The rigid aryl-aryl linkages facilitate coordination of the metals in positions prone to interaction with the central arene and also enforce a relatively large distance between donors, depending on ring substitution, favoring coordination of multiple metals. Further exploring the potential of phosphinoaryl-benzene frameworks to support discrete metal clusters with unusual bonding motifs, herein we present the synthesis and characterization of trinuclear Ni complexes displaying metal-metal bonds and strong metal-arene interactions.

Comproportionation reactions between  $\text{Ni}^0$  and  $\text{Ni}^{\text{II}}$  precursors have offered facile access to dinuclear  $\text{Ni}^{\text{I}}_2$  complexes.<sup>1f</sup> A similar strategy was employed toward multinuclear complexes. Treatment of a tris(phosphinoaryl)benzene species, **1**, with two equivalents of

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**Supporting Info.** Detailed experimental procedures, characterization data, and crystallographic details for complexes **2**, **3**, **4**, and **6** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Ni(COD)<sub>2</sub> (COD = cyclooctadiene) followed by one equivalent of NiI<sub>2</sub> afforded the trinickel species **2** (Scheme 1). A single crystal X-ray diffraction (XRD) study of complex **2** reveals a trimetallic complex with one phosphine arm coordinated per Ni center (Figure 1). Two metal centers (Ni1, Ni2) are bridged by an iodide and coordinated cofacially relative to the central arene. The third Ni (Ni3) is located on the opposite face relative to the central arene ring and coordinated by a terminal iodide. Complex **2** exhibits a short Ni1–Ni2 distance (2.3907(2) Å) similar to previously reported bonding Ni<sup>I</sup>–Ni<sup>I</sup> motifs<sup>1f, 1i, 4a, 5</sup> or metal-metal distances in [Ni<sub>3</sub>]<sup>2+</sup> species.<sup>6</sup> Additionally, strong metal-arene interactions to the central ring are observed, with Ni–C distances ranging between 1.95–2.11 Å.<sup>5a</sup> The solution <sup>1</sup>H nuclear magnetic resonance (NMR) spectrum of **2** shows peaks only in the diamagnetic region with significantly upfield shifted proton signals that correspond to the central ring at 4.61 and 3.35 ppm in 2:1 ratio, indicative of strong metal-arene interactions as shown by the crystal structure. The <sup>31</sup>P NMR spectrum of **2** in C<sub>6</sub>D<sub>6</sub> at room temperature displays two phosphorus signals: a triplet at 11.66 ppm and a broad multiplet at 67.71 ppm in 1:2 ratio. The upfield peak is assigned to the mononickel site, while the second peak corresponds to the dinuclear site. The presence of two rather than three peaks for the phosphines (<sup>31</sup>P NMR) and the hydrogen atoms of the central arene (<sup>1</sup>H NMR) suggests that although the solidstate structure has C<sub>1</sub> symmetry, the solution structure is fluxional. An exchange process consistent with the observed spectra involves shifting of the iodide and phosphine coordinated to Ni3 across a reflection plane perpendicular to the central ring and containing C2 and C5.

Previous studies of a dinuclear Ni complex supported by a related triphosphine demonstrated the reversible interconversion of isomers with the two metal centers coordinated to the same face vs. opposite sides of the central arene.<sup>4a</sup> Halide abstraction induced formation of the cofacial isomer with a Ni<sup>I</sup>–Ni<sup>I</sup> bond and a bridging halide. Analogously, complex **2** was treated with Tl(OTf) (OTf = triflate) in an attempt to generate a cationic triangulo trinickel cluster capped by a μ<sub>3</sub>-iodide. However, a dinuclear complex **3** (Scheme 1) was isolated as the major product, as revealed by XRD (Figure 1). Formation of **3** likely results from loss of an equivalent of Ni<sup>0</sup> following halide abstraction, consistent with the black precipitate observed during reaction. Attempts to regenerate **2** by addition of a third Ni center with Ni(COD)<sub>2</sub> in the presence of a halide do not lead to the trinuclear complex, suggesting that the formation of **3** is irreversible. The solid-state structure of **3** shows the two metal centers on opposite faces of the central arene. Ni1 is coordinated by two phosphines, and Ni2 by one phosphine and a terminal iodide. As with complex **2**, both metal centers interact strongly with the π system of the central ring, indicated by the short Ni–Carene distances of 1.97–2.17 Å. The <sup>1</sup>H NMR spectrum shows broad peaks in the diamagnetic region. Three upshifted signals for the central ring protons in a 1:1:1 ratio (4.5 – 6 ppm) are observed, consistent with the short Ni–Carene distances. Consistent with the low symmetry suggested by the <sup>1</sup>H NMR spectrum, the <sup>31</sup>P NMR spectrum displays three peaks in a 1:1:1 ratio. The NMR data are consistent with the solid-state structure of **3** having C<sub>1</sub> symmetry. The fluxional process exchanging the sides of the molecule as described for **2** is slower for **3**, although the broad peaks observed at room temperature approach to coalescence.

Complexes **2** and **3** represent unusual cases of electronic interactions between Ni centers and arenes. Previous examples of dinickel complexes with metal arene interactions are of three types. Complexes with cofacial Ni<sup>I</sup> centers display the metals in close proximity (2.3–2.6 Å) consistent with a Ni<sup>I</sup>–Ni<sup>I</sup> bonding interaction.<sup>1f, 4a, 5b, 7</sup> The metal-arene interactions in these complexes are typically supported by pendant donors, although a tetraphenylborate was reported to coordinate the Ni<sup>I</sup><sub>2</sub> moiety without additional ligands.<sup>7a</sup> A second type of Ni<sup>2</sup>–arene complex involves two Ni<sup>0</sup> centers ligated to opposite sides of the arene.<sup>5a, 8</sup> A third class includes dinickel complexes with metals coordinated on opposite faces of the arene,

but in higher oxidation states.<sup>4a,7b,9</sup> A common metal-arene binding mode in these complexes is  $\mu\text{-}\eta^3\text{:}\eta^3$ , with structural distortions of the ring away from planarity and elongation of the C–C bonds between the two  $\eta^3$  metal coordination sites.<sup>7b,9a</sup> This binding mode and the diamagnetism of these complexes has been interpreted as a formal reduction of the ring by  $\text{Ni}^{\text{I}}$  to result in a diallyl moiety and two  $\text{Ni}^{\text{II}}$  centers. For a related  $\mu\text{-}\eta^1\text{:}\eta^3$  binding mode, the two unpaired electrons of the  $\text{Ni}^{\text{I}}$  centers couple via a backbonding interaction with an empty arene  $\delta^*$  orbital different from the diallyl case, as supported by computation and the shortened C–C bonds adjacent to the  $\eta^3$ -coordinated moiety.<sup>4a</sup> Trinuclear complexes of Ni supported by interactions with an arene have not been structurally characterized to the authors' knowledge.<sup>10</sup> Compounds **2** and **3** both show distortion of the coordinated arene suggestive of a diallyl structure, with the elongated C–C bonds linking the allyl moieties (C1–C6 and C3–C4 *ca.* 1.46 Å). One allyl moiety coordinates to a monophosphinemononickel site, and the second binds either a diphosphine-mononickel (**3**) or a diphosphine-dinickel site (**2**). Compound **3**, binding the arene  $\mu\text{-}\eta^3\text{:}\eta^3$ , belongs to the third class of compounds described above. Compound **2**, binding the arene  $\mu^3\text{-}\eta^3\text{:}\eta^3$ , displays two metals instead of one coordinated to one of the allyl moieties. There is a single other complex that has been structurally characterized with a  $\mu^3\text{-}\eta^3\text{:}\eta^3$ -arene coordinated to three ruthenium centers.<sup>11</sup> In the limiting case of a doubly reduced arene, the mononuclear site corresponds to a  $\text{Ni}^{\text{II}}$  and the binuclear site to a  $\text{Ni}^{\text{I}}\text{-Ni}^{\text{I}}$  moiety. The  $\text{Ni}_2$  motif with bridging allyl ligands has been structurally characterized.<sup>12</sup> The strong interactions between the metal centers and the arene are not only supported by the short distances in the solid-state, but also by NMR spectroscopy.  $^{31}\text{P}\text{-}^{31}\text{P}$  coupling through five bonds is observed in both **2** and **3**, indicating electronic communication across metals coordinated to opposite faces of the arene.

While halide abstraction results in the loss of  $\text{Ni}^0$ , a cofacial trinickel complex (**4**) can be isolated from the reaction of complex **2** with  $\text{Na}_2\text{Fe}(\text{CO})_4$  (Scheme 1). The hexanes soluble fraction from this reaction shows one singlet in the  $^{31}\text{P}$  NMR spectrum at 61.90 ppm. The  $^1\text{H}$  NMR spectrum displays the central arene proton signal at 5.77 ppm, again indicative of strong metal-arene interactions and also suggesting a high symmetry structure. The solution infrared (IR) spectrum of **4** shows intense bands at 1846 and 1796  $\text{cm}^{-1}$ , consistent with  $\mu_2\text{-CO}$  ligation. In agreement, the XRD study of **4** reveals a *pseudo*- $C_3$ -symmetric structure, displaying a triangulo-trinickel core with each metal center coordinated by a phosphine donor, the arene moiety, and bridging  $\mu_2\text{-CO}$  ligands (Figure 2). The electron rich  $\text{Ni}_3^0$  core is stabilized by back-bonding to CO and arene. The solidstate structure of **4** shows different metal-arene interactions than **2**. In contrast to the  $\mu_3\text{-}\eta^3\text{:}\eta^3$  arene binding mode of **2**, complex **4** displays  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$  metal coordination to localized olefin moieties of the central arene. The bridging CO ligands likely provide additional stabilization to the  $\text{Ni}_3$  core that is not accessible from **2** by iodide abstraction, albeit in a different oxidation state. To generate **4**,  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  acts as both a reducing agent and CO source. A more direct route to **4** employing a  $\text{Ni}^0$  precursor was attempted. Treatment of **1** with  $\text{Ni}(\text{COD})_2$  and appropriate amounts of CO only resulted in the formation of a trinickel nonacarbonyl complex with each phosphine arm coordinating a  $\text{Ni}(\text{CO})_3$  unit rather than the arene-supported trinuclear cluster with Ni–Ni contacts (see SI).

Compound **4** represents the first structurally characterized example of arene-supported triangulo-nickel complex. A  $\text{Ni}_3$  cluster supported by the cyclooctatetraenyl dication has been reported.<sup>10</sup> Higher oxidation state  $\text{Ni}_3$  moieties are typically supported by cyclopentadienyl or  $\kappa^2$ -bridging ligands.<sup>13</sup> A notable difference compared to the majority of reported  $\text{Ni}_3$  species is the lack of a  $\mu_3$ -capping ligand besides the arene.

Typically, the  $\text{Ni}_3$  core is coordinated by two  $\mu_3$ -ligands such as alkyne,<sup>14</sup> CO,<sup>13a</sup> alkylidyne,<sup>15</sup> benzyne,<sup>16</sup> halide,<sup>6c</sup> chalcogenide,<sup>6d</sup> or hydride moieties. Beyond nickel,

trimetallic complexes supported by  $\mu_3$ -arene donors are known for Os,<sup>17</sup> Co,<sup>18</sup> Rh,<sup>19</sup> Ru,<sup>11</sup> and Pd.<sup>20</sup> Given the unusual binding mode for Ni in the trimetallic complex **4**, the versatility of such coordination mode was investigated with fewer phosphine donors linked by a central arene. A *para*-terphenyl diphosphine was employed as supporting ligand (Scheme 2).<sup>1f</sup> Metallation of **5** with three equivalents of Ni(COD)<sub>2</sub> in the presence of a slight excess of carbon monoxide provided access to the desired trinickel complex, **6** (Scheme 2) in 74% yield. Control of carbon monoxide stoichiometry is necessary as a large excess results in the excessive coordination of carbon monoxide to generate previously characterized transfacial dinuclear Ni(CO)<sub>n</sub> (n = 2-3) complexes.<sup>1f</sup> An XRD study reveals that complex **6** has similar structural features to **4** in terms of the trinuclear core (Figure 2). Instead of a third phosphine arm, Ni3 binds a terminal CO ligand. Consistent with the solid-state structure, the solution IR spectrum of **6** shows bands at 1985, 1864, and 1817 cm<sup>-1</sup> indicative of terminal and bridging carbon monoxide coordination.<sup>21</sup> The facile over carbonylation with the triphosphine ligand (**1**) suggests that the more flexible methylene-linked phosphine arms do not stabilize the intermediates and metal arene interactions that facilitate formation of the Ni<sub>3</sub> core to the same extent as **5**. Complex **4** and **6** exhibit average Ni–Ni distances of 2.44 Å and 2.45 Å, respectively, that are similar to a previously reported Ni<sup>0</sup>–Ni<sup>0</sup> motif (2.47–2.50 Å) in a Ni<sub>4</sub>(CO)<sub>6</sub>(PMe<sub>3</sub>)<sub>4</sub> cluster.<sup>22</sup> The Ni–Ni distances of **4** and **6** are also similar to those of the Ni<sub>3</sub>(dppm)<sub>3</sub> (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) clusters that are more oxidized.<sup>6c,23</sup>

The terminal carbon monoxide ligand of complex **6** is readily substituted upon addition of trimethylphosphine (PMe<sub>3</sub>) to yield complex **7** (Scheme 2). While single crystals suitable for X-ray diffraction studies have not been obtained to date due to the compound's high solubility, spectroscopic characterization of the complex indicates an intact triangulo-trinickel core. The C<sub>s</sub> symmetry of complex **6** has not been perturbed by PMe<sub>3</sub> substitution as two <sup>1</sup>H NMR resonances corresponding to the methine protons are observed (2.41 and 2.24 ppm). The <sup>31</sup>P NMR spectrum of **7** displays the terphenylphosphines as a doublet at 51.49 ppm and the PMe<sub>3</sub> as a triplet at –6.61 ppm; the observed multiplicity is consistent with the assigned structure. Strong metal-arene interactions are also maintained based on the upfield-shifted <sup>1</sup>H NMR resonances at 5.12 and 4.67 ppm. The substitution of the terminal CO ligand is supported by the IR spectrum showing only bands indicative of bridging CO ligands (1854, 1783 cm<sup>-1</sup>) and the disappearance of the peak at 195.08 ppm (<sup>13</sup>C NMR) observed for complex **6**. The increased electron density of Ni3 induced by the ligand substitution is reflected in the 0.53 upfield shift of the arene C–H <sup>1</sup>H NMR peak compared to **6** and the lower stretching energy of the bridging CO ligands. The coordination sphere of the Ni<sub>3</sub> cluster is identical in complexes **4** and **7**. In agreement, the CO stretching frequencies observed for the two compounds are almost identical (1847, 1795 cm<sup>-1</sup> for **4**). The lability of this terminal CO ligand suggests that coordination and activation of other molecules at the Ni<sub>3</sub> unit in **6** may be possible.

In summary, bi- and trinuclear Ni complexes have been synthesized by employing phosphine ligand architectures that facilitate metal-arene interactions. Two complexes with metal centers coordinated transfacially show structural features consistent with a diallyl motif for the bridging arene. <sup>31</sup>P–<sup>31</sup>P NMR coupling across five bonds spanning the bridging arene are indicative of the strong interactions with the metals. Cofacial trinuclear Ni<sub>3</sub> complexes have been isolated as well, and exhibit  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$  arene binding, a novel coordination mode for nickel. The triangular Ni<sub>3</sub> moiety was supported by the diphosphine **5**, in addition to the triphosphine **1**, suggesting that the arene-Ni<sub>3</sub> motif does not require pendant donors for each Ni center. Facile ligand substitution was observed for the terminal CO ligand of the Ni<sub>3</sub> species **6**. The present complexes demonstrate the utility of a coordinating arene as a versatile multidentate ligand design element for the synthesis of new types of metal clusters.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

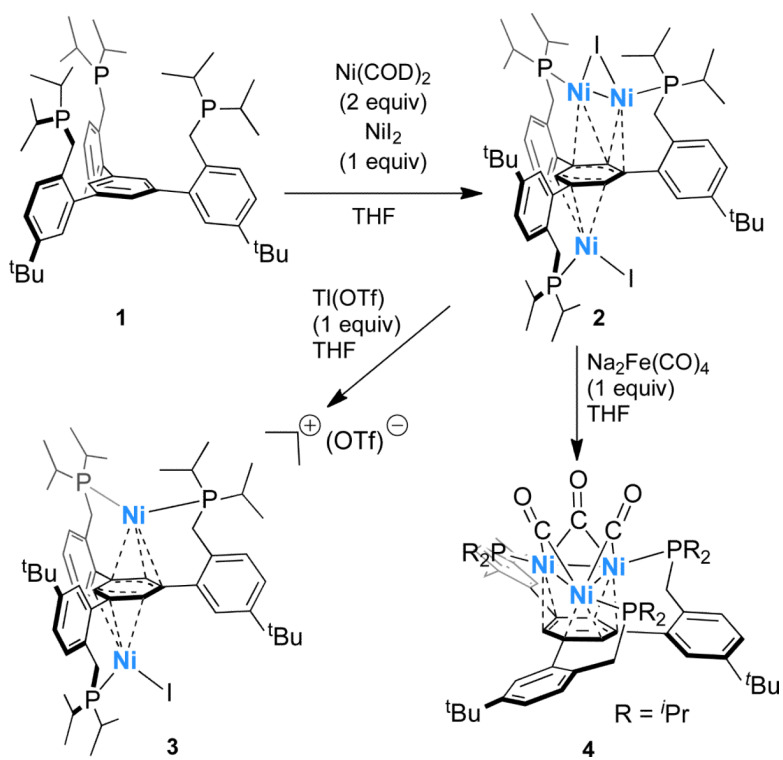
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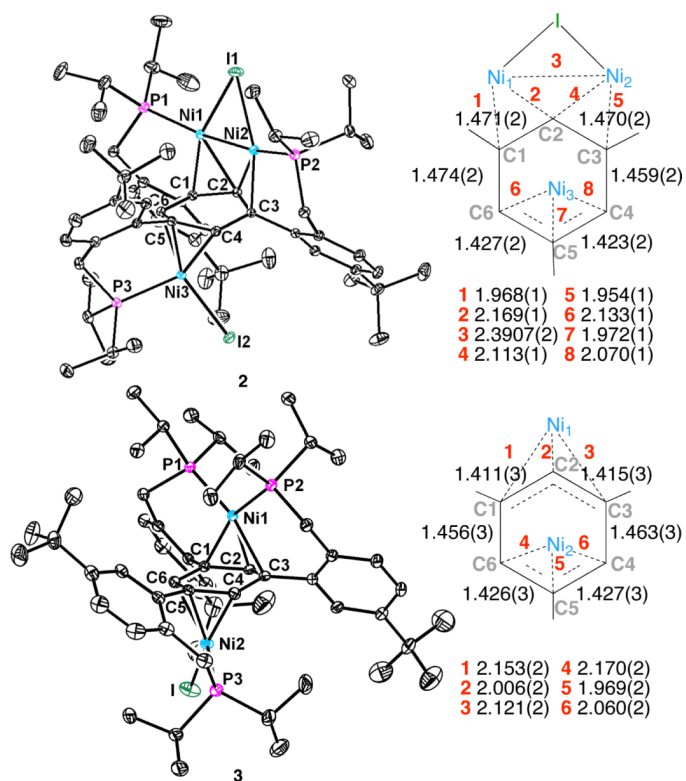
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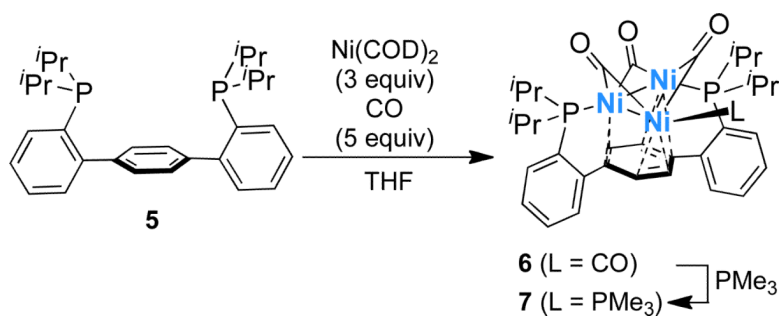


**Scheme 1.**  
Synthesis of di- and trinickel complexes supported by triphosphine-arene framework (1)

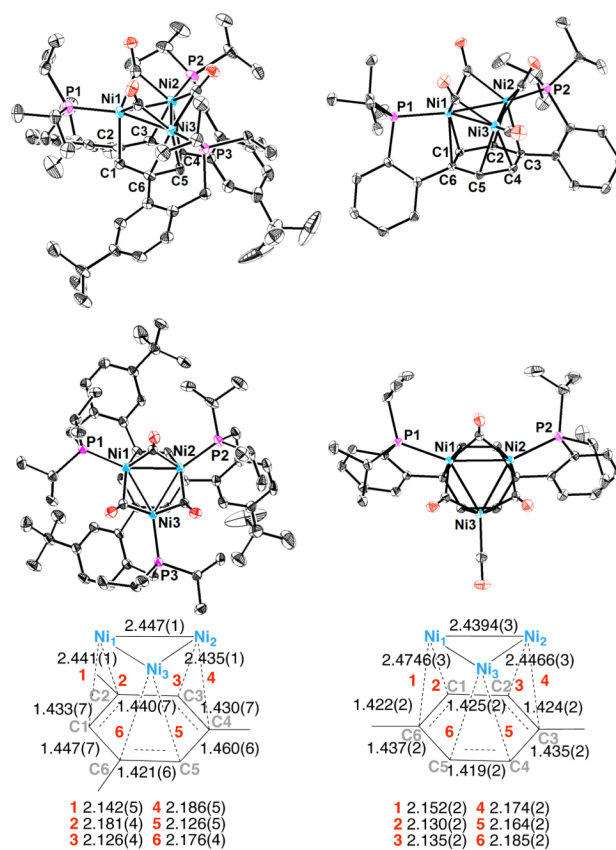


**Figure 1.** Solid-state structures with thermal ellipsoids at the 50% probability level (left) and selected C–C and Ni–C bond distances (Å, right) of **2** (top) and **3** (bottom). Hydrogen atoms and anions are omitted for clarity.



**Scheme 2.**

Synthesis of triangulo-trinickel complexes supported by a diphosphine ligand



**Figure 2.** Solid-state structures with thermal ellipsoids at the 50% probability level (*top*: side view; *middle*: top view) and selected C–C and Ni–C bond distances (Å, bottom) of **4** (left) and **6** (right). Hydrogen atoms are omitted for clarity.